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BATCH COPPER ION BINDING AND EXCHANGE PROPERTIES OF PEAT

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Abstract—Cupric ion fixation by raw peat is likely involved in both cation exchange with H^+, Ca^{2+}, Mg^{2+} and adsorption–complexation, i.e. fixation of the same equivalent of copper ions and anions (NO_3^-) without any ion release. The importance of both reactions depends largely on initial copper concentration, peat type and pH. Isotherms of copper (initial concentration ranging between 1 and 20 mM) fixation on two types of peat (eutrophic and oligotrophic peat at 30 g d.w./l at pH ranging between 2 and 4) showed that the higher the initial cupric concentration, the more important is this complexation reaction; over this initial cupric concentration range, ion exchange sites were relatively saturated and reached 308 and 101 mmol/kg d.w. for eutrophic and oligotrophic peat whereas no saturation was found for complexation sites, their capacity attaining up to 74 and 119 mmol/kg d.w., respectively.

The apparent equilibrium constant for ion exchange with acid-treated peat (initial pH 4.0, 30 g d.w./l) for various metal binding on both peat sites ranged between 1.1 and 10.8 in 15 mM metallic solutions. The apparent affinity in batch conditions for 5 elements may be compared according to the apparent global equilibrium constants, ranging between 1.1×10^{-6} and 20.2×10^{-6}: Pb > Cu > Ca > Mg, Zn for eutrophic peat and Pb > Ca > Cu > Mg, Zn for oligotrophic peat.

Key words—peat, metal cation, ion exchange, adsorption, complexation equilibrium, electroneutrality

INTRODUCTION

Peat has long been recognized as a natural humic substance trapping cations (Bunzl, 1974; Bunzl *et al.*, 1976). Its carboxylic, phenolic and hydroxylic functional groups play ion exchange and complexation roles during the fixation of metal ions from solution (Smith *et al.*, 1977; Bloom and McBride, 1979). Batch experiments and assays using columns have been extensively exploited by Aho and Tummavuori (1984) and Ansted and MacCarthy (1984) so as its application for the treatment of metal-containing effluents in industry (Coupal and Lalancette, 1976). As far as the mechanism of reaction between ionic metal and peat is concerned, results seem very different according to the peat used. Some authors like Aho and Tummavuori (1984) and Bunzl *et al.* (1976) have found that only ion exchange exists, one divalent metal ion being exchanged with two hydrogen ions. Other authors have reported that the mechanism is both ion exchange and complexation (Coleman *et al.*, 1956). With the same peat samples used in this work, i.e. eutrophic "Heurteauville" and oligotrophic "Floratorf" types, Gosset (1986) has concluded that complexation mainly occurs during metal fixation by peat but he found later (Gosset *et al.*, 1986), during experiments of metal desorption by HCl (pH 1.5) in columns, that ion exchange between H^+ and metal cations occurred and that about 90% of metal cations were displaced from these peat exchangers. The same desorption results were also reported by Bunzl *et al.* (1976) and Dissanayake and Weerasooriya (1981). But a measure of hydrogen ions release is not sufficient to study the phenomenon of ion exchange especially when raw peats are used, since other metal cations may have been adsorbed previously in its natural environment. The purpose of the work is to evaluate the ion exchange and complexation properties of peats in batch with a complete balance of anion and cation exchanges during cupric ion fixation.

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MATERIALS AND METHODS

Peat samples and chemical reagents

Two types of peat were used, an eutrophic peat called "Heurteauville", which contained 80% water, and an oligotrophic one called "Floratorf", with 50% water, both being commercially available in France for agriculture purpose.

Eutrophic peat was formed in alluvial plains supplied by well mineralized water. This kind of peat is poor in cellulose but rich in humic substances. Oligotrophic peat is a sphagnum one which is more acid than eutrophic peat and contains more organic matter than the first. Both peats containing about 75–85% humic acid and 15–25% fulvic acid.

Two methods of peat pre-treatment were used for this study compared to raw peat with no pre-treatment:

(a) acid treatment, i.e. raw peat samples were shaken vigorously in 100 ml of 1 N HCl in polyethylene bottles for several hours until no cation release was observed and repeated washings with distilled water were followed till the pH of peat suspensions reached 4.0; at each step peat samples and supernatants were separated by centrifugation;
(b) thermal treatment, i.e. 24 h drying at 100°C.

Metallic salts used in this work were cupric and lead nitrate and zinc, calcium and magnesium chlorides. All metallic salts and chemical were of analytical grade (Prolabo P.A., Paris, France).

Solution analysis

Concentration of metallic cations was determined by acetylene–air flame atomic absorption spectrophotometry (Perkin–Elmer 2380) with single element hollow cathode lamps.

Concentration of nitrates was determined by potentiometry using a nitrate specific electrode (pNO_3) and a Ag/AgCl reference electrode connected to an ionometer (SOLEA-TACUSSEL IONOMATE 80, Villeurbanne, France) and a programmable HP 70S calculator. A colorimeter (SKALAR Model 5100) linked with an automatic sampler (Sampler 1000) and a calculator (Data system 8500/01) was also used for nitrate analysis during the determination of fixation isotherms and of pH dependence of these equilibria. Concentration of Cl^-, if necessary, was determined by $AgNO_3$ titration method.

Proton exchangeable metallic cations in raw peat

Two samples of 3 g dry weight (d.w.) raw peat (eutrophic or oligotrophic) were mixed into 100 ml of 2 M HCl. Peat suspensions were shaken for 24 h at room temperature. Supernatants were separated by centrifugation at 6000–8000 rpm during 5–10 min. Amounts of metal cations were determined in supernatants and expressed in mg/kg d.w. or mequiv/kg d.w.

Procedure for metal fixation by peat

Peat samples were swollen and homogenized with 100 ml of distilled water during 24–48 h followed by centrifugation or vacuum filtration to withdraw supernatants. The same concentration of peat, i.e. 30 g d.w./l (3 g dry weight peat in 100 ml cupric solution or 1.5 g dry weight in 50 ml solution) was used for all experiments. In order to observe more correctly ion exchange between metal ions and H^+, the pH of cupric solutions was adjusted to the same level as peat suspension by addition of 0.1 N NaOH or HCl solutions except for the experiment of pH influence on copper fixation. Ninety min of contact time were chosen since we have found previously that in such conditions, equilibrium was reached within a couple of minutes (Chen, 1986; Kadlec and Keoleian, 1986).

(a) Copper fixation reactions by peat. Three grams of raw peat (on the basis of dry weight) were introduced into 100 ml of 10 mM cupric solution. Peat suspensions were stirred during 90 min and centrifuged at 4800–8500 *g* for 10 min. The initial and final concentrations of Cu^{2+}, Ca^{2+}, Mg^{2+}, H^+ and NO_3^- were measured except for the initial concentration of NO_3^- which was calculated form initial cupric nitrate concentration: over the pH and concentration range investigated, we observed that copper nitrate in the initial solution contains only Cu^{2+} and NO_3^- ions. The amount of fixed and released ions were determined on supernatants.

(b) Influence of initial cupric concentration upon its fixations. Eight samples of heat-treated dry eutrophic peat (30 g/l) previously swollen with distilled water were mixed with 8 samples of 50 ml cupric solution (initial pH 5.0), initial concentration of which ranged between 0 and 20 mM. Temperature was fixed at about 20°C. After 90 min contact time of peat and metal solution, the liquid and solid phases were separated by vacuum filtration and the supernatants were collected. Concentrations of H^+, Ca^{2+}, Cu^{2+}, Mg^{2+} and NO_3^- at equilibrium were measured on supernatants.

Eight samples were used for the heat-treated oligotrophic peat (30 g/l) experiment. The same experimental conditions were employed except for the initial pH which was adjusted to 3.5 because this is its natural value when oligotrophic peat is swollen in distilled water. The concentration of NO_3^- was determined by colorimetry and concentrations of H^+, Ca^{2+} and Mg^{2+} measured by atomic absorption spectrophotometry as described above.

(c) Influence of initial pH on copper fixation. Five samples of heat-treated peat (1.5 g, eutrophic pH 5.0 or oligotrophic pH 3.5) pre-homogenized in distilled water were mixed into 5 samples of 50 ml (10 mM) cupric solution, the pH of which was adjusted to 1.7, 3, 4, 5 and 6, respectively. After 90 min equilibration, supernatants were vacuum filtrated and collected for cations and anion analysis.

(d) Apparent equilibrium constant determination. Five samples of acid-treated peat (3 g dry weight), whose pH reached 4.0 when swollen in distilled water for several hours, were mixed with 5 selected metal solutions, each containing one of the following cations: Pb^{2+}, Cu^{2+}, Mg^{2+}, Ca^{2+} and Zn^{2+} (15 mM, initial pH 4.0) at room temperature. Supernatants were analysed for cations and anions.

To evaluate the total amount of sites of fixation, we added peat samples, previously equilibrated with 15 mM metallic solution and separated from supernatant, into 100 ml of 600 mM of each selected metal solution over initial pH range 3.1–3.5: cupric concentration was measured in supernatant solution after 90 min contact time.

RESULTS AND DISCUSSION

Proton exchangeable cations in raw peats

Amounts of metallic cations released by two types of peat when suspended in 2 M HCl solution are summarized in Table 1. Eutrophic peat contains much more calcium (1250 mequiv/kg d.w.) and iron (289 mequiv/kg d.w.) than oligotrophic peat (60 and 23.7 mequiv/kg d.w., respectively). Both types of peat have a similar level of magnesium, sodium and potassium. There are few exchangeable heavy metals

Table 1. Proton exchangeable metal cations in eutrophic and oligotrophic raw peat: mean value of cation released by two samples of 3 g d.w. peat suspended in 100 ml 2 M HCl solutions during 24 h. All metal cation releases are referred to as peat dry weight in samples

Eutrophic peat:												
Element	Na	K	Ca	Mg	Fe	Ni	Cu	Zn	Pb	Cr	Cd	Total
mg/kg	336.7	265.0	25000	1000	5400	33.3	16.7	13.3	6.7	31.7	0	32103
mequiv/kg	14.6	6.8	1250	83.4	289.2	1.14	0.52	0.40	0.06	1.22	0	1650
Oligotrophic peat:												
Element	Na	K	Ca	Mg	Fe	Ni	Cu	Zn	Pb	Cr	Cd	Total
mg/kg	466.3	202.0	1200	870	440	30.0	16.7	13.3	41.7	23.3	0	3303
mequir/kg	20.3	5.2	60	72.6	23.7	1.14	0.52	0.40	0.40	0.90	0	185

(0–1.2 mequiv/kg d.w.), in accordance to previous results by Glooschenko and Capoblanco (1982) using a mineralization method on a Canada peat.

This experiment shows that a total equivalent of 185 and 1650 mequiv/kg d.w. cations occupy ion exchange sites in eutrophic and oligotrophic peat, respectively: these sites could probably participate in cation exchange when peat is in contact with a metal solution such as a cupric one, as noted by Kadlec and Keoleian (1986).

Properties of copper fixation by peat

The phenomenon of ion exchange between copper ions and calcium in eutrophic peat and magnesium or calcium in oligotrophic peat was observed by Gangiotti *et al.* (1986): he found that the number of equivalent released cations is always inferior to that of fixed copper, indicating that a reaction mechanism different to ion exchange may exist. An analysis of nitrate ion exchange accompanying copper fixation may be an effective way to study such adsorption–complexation mechanisms. Table 2 presents results of reaction between peat (30 g d.w./l) and cupric nitrate solution by monitoring Cu^{2+} Ca^{2+}, Mg^{2+} H^+ and NO_3^- levels in initial and final equilibrium supernatant solutions.

Solution electroneutrality may be expressed by the A ratio of anion and cation equivalent concentrations at equilibrium:

$$A = \frac{(NO_3^-)}{(H^+) + 2(Ca^{2+}) + 2(Mg^{2+} + 2(Cu^{2+})} \quad (1)$$

where ( ) refers to molar concentration. As this A ratio only takes into account nitrate anion, any anion exchange will yield A values lower than 1. On the contrary A values larger than 1 would indicate that cation exchange with species may not be taken into account in this charge balance. As shown on Table 2, A values equal, under such concentration and pH conditions, 0.86 for eutrophic and 0.88 for oligotrophic peat, indicating that some limited anion exchange happened. Simultaneously a non-negligible amount of NO_3^- was fixed on peat. It seems very likely that an equivalent amount of copper was fixed by peat in order to balance that negatively charged ions fixation: this property could be called molecular complexation of copper on peat. From the reaction of eutrophic peat with 10 mM cupric solution (final pH 4.0), 0.403 mmol of NO_3^- were fixed: thus the amount of copper fixed with NO_3^- was assumed to be 0.403 mequiv/kg. The total amount of fixed copper was equal to 1.933 mequiv, 1.53 mequiv copper was fixed by cation exchange. The amount of Ca^{2+}, Mg^{2+} and H^+ released during that Cu^{2+} cation exchange was $(2 \times 7.55) + (2 \times 0.57) + 0.09 = 16.3$ mequiv/l or 1.63 mequiv in the 100 ml solution. Both figures, i.e. 1.53 and 1.63 mequiv, being close to each other within experimental error of such determination, we think that the second part of copper fixed on peat, i.e. 1.53 mequiv, is indeed related to ion exchange. The reaction of copper ion with peat would thus be both ion exchange and adsorption–complexation. The amount of copper fixed by ion exchange reaches 84% under these experimental conditions. We will see below that this amount varies with free copper concentration or pH within the solution.

Similar results were found with 30 g d.w./l oligotrophic peat at 2.5 final pH equilibrated with 10 mM cupric nitrate solution: 55% of copper fixed was attributed to ion exchange and 45% to copper complexation.

As pointed out by Coupal and Lalancette (1976), peat is a rather complex material containing lignin and cellulose as major constituents. Peat carboxylic and phenolic groups are likely to be involved in chemical bonding. Cornell (1983) has shown that its microporosity varies with swelling: this porosity could explain high adsorption reactions yielding metal fixation capacities much larger than ion exchange capacities.

Influence of copper concentration upon its fixation by peat

Metal fixation isotherm (0–20 mM cupric nitrate solution and 30 g d.w./l of eutrophic peat with initial pH 5.0) shows us that there is no apparent saturation over that copper concentration range [Fig. 1(a)]. This result is in accordance with previous results obtained by Gosset *et al.* (1986), Gosset (1986), Gangiotti *et al.* (1986) and Gangneux *et al.* (1985) with the same material. The isotherm curve, however, could be split according to the type of reaction occurring: the

Table 2. Reaction in batch between 30 g d.w./l raw peat and 10 mM cupric ions

		Cu^{2+}	Ca^{2+}	Mg^{2+}	H^+	NO_3^-	A
Eutro.	C_i (mM)	10.03	0.72	0	0.01 pH = 5.0	20.06*	0.86
	C_e (mM)	0.38	8.27	0.57	0.10 pH = 4.0	16.03	
Oligo.	C_i (mM)	9.69	0.87	0	0.32 pH = 3.5	19.38*	0.88
	C_e (mM)	5.35	0.87	0.75	3.39 pH = 2.5	15.25	

C_i = initial concentration.
C_e = concentration at equilibrium.
*Value calculated from initial cupric nitrate concentration.
Eutro. = eutrophic peat.
Oligo = oligotrophic peat.
A = ratio of electroneutrality, i.e. anion/cation equivalent concentration ratio.

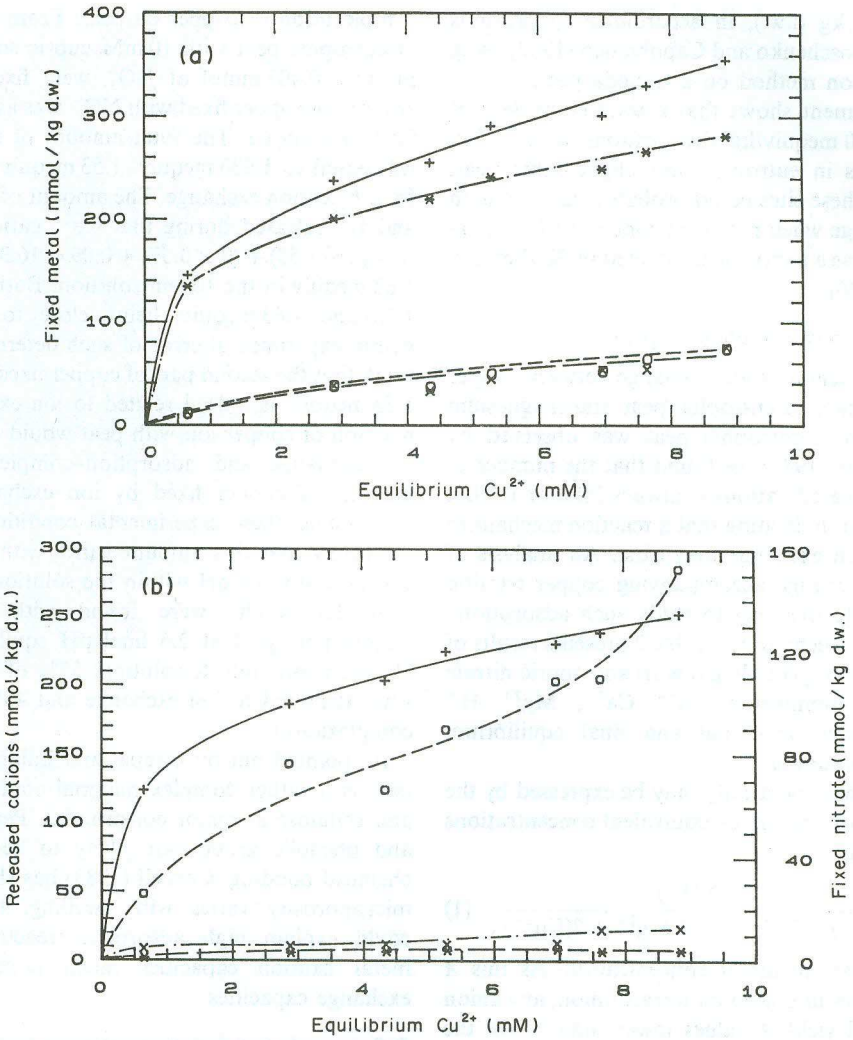

Fig. 1. (a) Influence of free copper content on amount of metal fixed on eutrophic peat. +, Total copper fixation; ✻, fraction of copper fixed by ion exchange; ○, ×, fraction of copper fixed by complexation using two approaches: ○, calculated by subtracting ion-exchanged cupric ions from total amount of fixed copper; ×, calculated from fixed nitrate ion amount. 1.5 g d.w. eutrophic peat equilibrated with 50 ml of cupric solution in the 0–20 mM initial range at initial pH 5.0 and final pH ranging from 3.6 to 5.0. (b) Influence of free cupric concentration on cation release and nitrate fixation on eutrophic peat. +, Calcium ion release; ×, magnesium release; ✻, proton release; ○, nitrate fixation. 1.5 g d.w. eutrophic peat equilibrated with 50 ml of cupric solution in the 0–20 mM initial range at initial pH 5.0 and final pH ranging from 3.6 to 5.0.

fixation due to ion exchange, determined by the number of equivalents of released cations (H^+, Ca^{2+}, Mg^{2+}), and the fixation due to complexation. The latter was determined using two methods: subtraction of ion exchange fraction from total fixed copper (in mmol/kg d.w.) or use of nitrate fixation for evaluating copper complexation; as shown on Fig. 1(a) both methods gave very similar results. Obviously both approaches could not be used if the A value of electroneutrality ratio had not been verified to be equal to 1. In fact, the A value, calculated from equation (1), ranged between 0.99 and 1.0 for all the points in Fig. 1(a). The ion exchange sites were relatively saturated and reached 280 mmol/kg d.w. whereas complexation ones reached only 0 and 21% in 0.5 and 9.0 mM free cupric solutions. This suggests that the amount of ion exchange sites is limited. Thus, complexation would be responsible for the non-saturation of isotherms. We will see later that, in 450 mM free cupric solutions, complexation is responsible for 90% of total copper fixed on peat. The final pH of these samples ranges between 4.2 and 3.57, with the lowest values corresponding to the highest initial cupric concentrations. But this amount of H^+ concentration variation is negligible (10 mmol/kg d.w.) compared with that of fixed copper (280 mmol/kg d.w.) and released calcium (250 mmol/kg d.w.) [Fig. 1(b)]. A small amount of magnesium release was also observed. On the contrary, ion exchange between copper ions and calcium plays an important role, indicating that ion exchange of raw eutrophic peat mainly occurs

between Cu^{2+} and Ca^{2+}. Nitrate fixation was observed to increase with cupric concentration: this was used to evaluate copper complexation shown in Fig. 1(a) curve (×).

Similar behaviour was found with oligotrophic peat samples (0–20 mM initial cupric concentration and 30 g d.w./l peat, initial pH 3.5): no apparent saturation of peat occurred in that copper concentration range and copper complexation seemed to be responsible for this non-saturation isotherm [Fig. 2(a)]. The electroneutrality A values reached 0.95–1.1. Different from experiments with eutrophic peat, copper complexation became more important than ion exchange when free copper content was superior to 6 mM. An excellent accord was observed with both methods to evaluate complexation reactions. Here the final pH ranged between 2.5 and 3.5 and this H^+ release was important: indeed ion exchange takes place essentially between copper ions and H^+ [Fig. 2(b)]. Besides, magnesium and calcium ions are also partially responsible for this ion exchange mechanism. A plateau was found for Ca^{2+} and Mg^{2+} release, 25 and 20 mmol/kg d.w., respectively, over this cupric concentration range. A fixation of NO_3^- was observed, showing that the amount of fixed NO_3^- increased regularly with increasing initial cupric concentration.

Langmuir and Freundlich equations may be used to evaluate ion exchange and complexation isotherms. For a saturation-type curve of ion

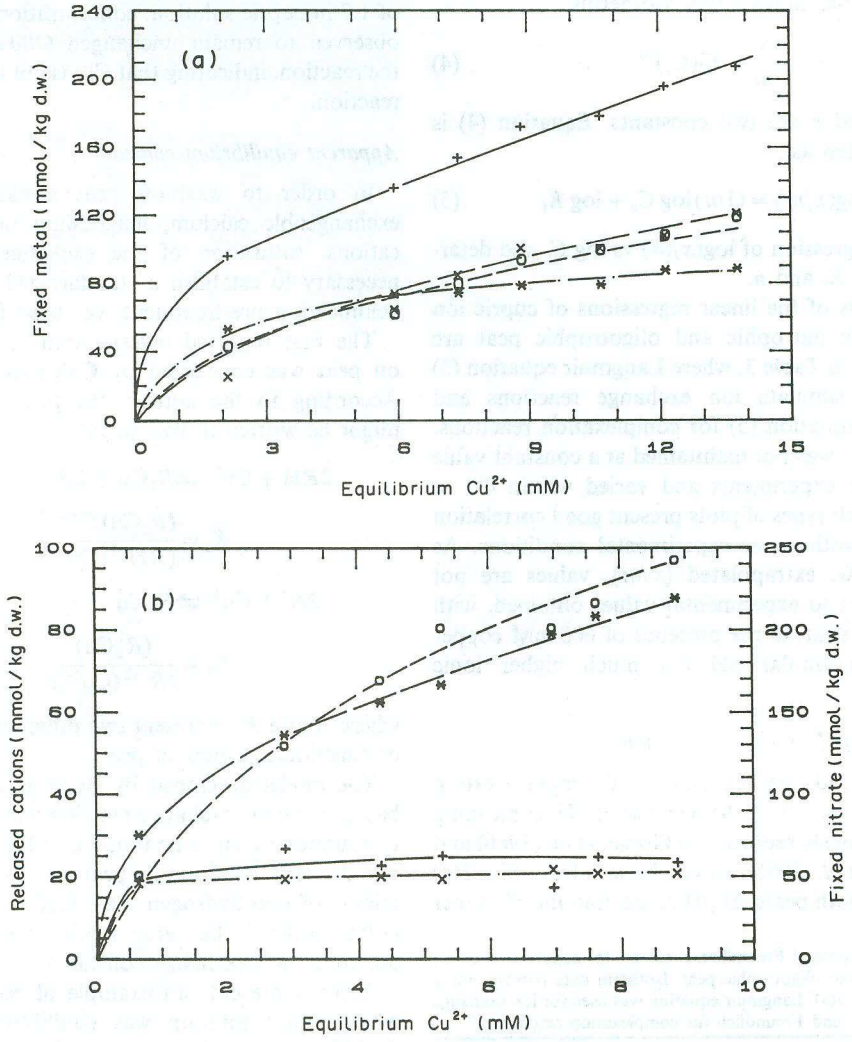

Fig. 2. (a) Influence of free copper content on amount of metal fixed oligotrophic peat. +, Total copper fixation; ✻, fraction of copper fixed by ion exchange; ○, ×, fraction of copper fixed by complexation using two approaches: ○, calculated by subtracting ion-exchanged cupric ions from total amount of fixed copper; ×, calculated from fixed nitrate ion amount. 1.5 g d.w. oligotrophic peat equilibrated with 50 ml of cupric solution in the 0–20 mM initial range at initial pH 5.0 and final pH ranging from 2.5 to 5.0. (b) Influence of free cupric concentration on cations release and nitrate fixation on oligotrophic peat. +, Calcium ion release; ×, magnesium release; ✻, proton release; ○, nitrate fixation. 1.5 g d.w. oligotrophic peat equilibrated with 50 ml of cupric solution in the 0–20 mM initial range at initial pH 5.0 and final pH ranging from 2.5 to 3.5.

exchange fraction, the Langmuir equation might be used, which is expressed as:

$$\frac{x}{m} = \frac{b(x/m)_0 C_e}{1 + bC_e} \quad (2)$$

where x/m represents fixed copper in mmol/kg d.w., C_e being free cupric concentration in mM and b referring to the Languir constant, $(x/m)_0$ being maximum capacity to fix copper. Equation (2) is usually transformed to (3):

$$\frac{C_e}{(x/m)} = \frac{1}{(x/m)_0} C_e + \frac{1}{b(x/m)_0} \quad (3)$$

for linear regression of $C_e/(x/m)$ vs C_e and determination of $(x/m)_0$ and b.

The Freundlich equation is generally used to describe non-saturation-type isotherms:

$$\frac{x}{m} = K_f(C_e)^{1/n} \quad (4)$$

where K_f and n are two constants. Equation (4) is usually written as:

$$\log(x/m) = (1/n)\log C_e + \log K_f \quad (5)$$

for linear regression of $\log(x/m)$ vs $\log C_e$ and determination of K_f and n.

The results of the linear regressions of cupric ion isotherms on eutrophic and oligotrophic peat are summarized in Table 3, where Langmuir equation (3) is used to simulate ion exchange reactions and Freundlich equation (5) for complexation reactions. Although pH was not maintained at a constant value during these experiments and varied within 0.7 to 1.0 units, both types of plots present good correlation coefficients within our experimental conditions. As shown below, extrapolated $(x/m)_0$ values are not very different to experimental values obtained, with acid-treated peat, in the presence of 600 mM copper solutions at similar pH but much higher ionic strength.

Influence of pH on copper fixation

We observed that capacities of copper fixation generally increase with the increase of pH, confirming results previously reported by Gosset *et al.* (1986) and Gangneux *et al.* (1985). As can be seen from Figs 3(a) and (b) for both peats, at pH 2, the amount of copper fixation is much lower (147 and 57 mmol/kg d.w. for eutrophic and oligotrophic peat, respectively) than that at pH 3. At initial pH_i 1.7, both cupric ions and protons compete for ion exchange sites and an increase of pH was thus observed: equilibrium pH_e reaching 2.54 and 2.10 in the supernatant for eutrophic and oligotrophic peat, respectively. Ion exchange and complexation fraction curves show that ion exchange is more pH dependent than complexation.

Table 3. Langmuir and Freundlich constants for copper fixation on raw eutrophic and oligotrophic peat. Isotherm data corresponding to Figs 1(a) and 2(a). Langmuir equation was used for ion exchange reactions and Freundlich for complexation reactions

	Langmuir: ion exchange			Freundlich: complexation		
	$(x/m)_0$ (mmol/kg)	b (mM^{-1})	r^*	K_f	$1/n$	r^*
Eutro.	308	0.74	0.99	15.1	0.69	0.99
Oligo.	101	0.44	0.99	25.1	0.56	0.98

r^* = correlation coefficient.
Eutro. = eutrophic peat.
Oligo. = oligotrophic peat.

Electroneutrality A values from equation (1) were found to be quite satisfactory, ranging between 0.94 and 1.1 over the pH range investigated, except for the 1.28 value obtained at pH_e 2.1 with oligotrophic peat. The concentration of Cl^- was taken into account in determining A values at the lowest pH values since HCl was added to reach a pH_i of 1.7 in cupric solution: concentrations of Cl^- were observed to remain unchanged (700 mg/l) through the reaction, indicating that Cl^- is not involved in the reaction.

Apparent equilibrium constant

In order to wash-off peat samples from any exchangeable calcium, magnesium or other metal cations, saturation of the exchanger by HCl is necessary to establish a standardized system. Thus acidification pre-treatment was used for this study.

The first reported investigation of ion exchange on peat was conducted by Coleman *et al.* (1956). According to the author, the peat–Cu^{2+} reaction might be written in two ways:

$$2RH + Cu^{2+} \rightleftharpoons R_2Cu + 2H^+ \quad (6)$$

$$K_1 = \frac{(R_2Cu)\,(H^+)^2}{(RH)^2\,(Cu^{2+})} \quad (7)$$

$$2R' + Cu^{2+} \rightleftharpoons R'_2Cu \quad (8)$$

$$K'_f = \frac{(R'_2Cu)}{(R')^2\,(Cu^{2+})} \quad (9)$$

where R and R' represent two different reactive sites or functional groups of peat.

The model developed by Bunzl *et al.* (1976) was based on an ion exchange reaction and is thus similar to equation (6) since he found that the adsorption of one divalent metal ion by peat was coupled with the release of two hydrogen ions. Kadlec and Keoleian (1986) utilized the same mechanism as Bunzl to determine ion exchange constants.

Table 4 presents an example of results obtained when cupric solution was equilibrated with pre-acidified peat. It demonstrates that with both peat types, the processes are the same as with raw peat: A values reach 1.03 with the eutrophic peat and 1.01 with the oligotrophic one, indicating an absence of anion exchange. An ion exchange reaction occurs between Cu^{2+} and H^+, but some nitrate ion depletion shows that complexation is also occurring with pre-acidified ion exchange peat samples.

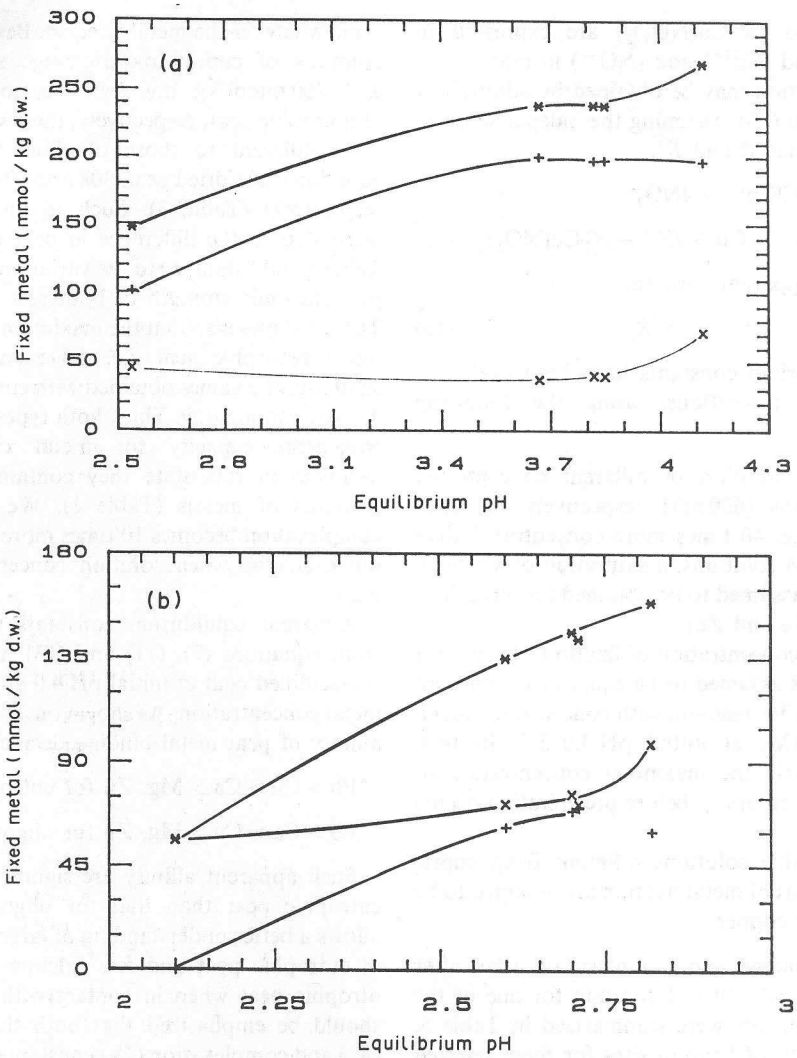

Fig. 3. (a) Influence of pH on copper fixation. ✱, Total fixed copper; +, copper fixed by ion exchange; ×, copper fixed by complexation. 1.5 g d.w. eutrophic peat equilibrated with 50 ml 10 mM cupric solution for initial pH ranging from 1.7 to 6.0. (b) Influence of pH on copper fixation. ✱, Total fixed copper; +, copper fixed by ion exchange; ×, copper fixed by complexation. 1.5 g d.w. oligotrophic peat equilibrated with 50 ml 10 mM cupric solution for initial pH ranging from 1.7 to 6.0.

Reactions have been expressed by equation (6). Reaction (8) was modified for complexation reactions, considering NO_3^- fixation:

$$2R' + Cu^{2+} + 2NO_3^- \rightleftharpoons R'_2Cu(NO_3)_2 \qquad (10)$$

with apparent constant:

$$K_2 = \frac{(R'_2Cu(NO_3)_2)}{(R')^2\,(Cu^{2+})\,(NO_3^-)^2} \qquad (11)$$

Table 4. Reaction in batch between 30 g d.w./l pre-acidified peat and 10 mM copper ions

		Cu^{2+}	Ca^{2+}	Mg^{2+}	H^+	NO_3^-	A
Eutro.	C_i (mM)	14.74	0.27	—	0.10 pH = 4.0	29.48*	1.03
	C_e (mM)	6.59	0.26	—	9.33 pH = 2.03	23.66	
Oligo.	C_i (mM)	14.52	—	0	0.10 pH = 4.0	29.04*	1.01
	C_e (mM)	8.93	—	0.01	5.56 pH = 2.25	23.73	

C_i = initial concentration.
C_e = concentration at equilibrium.
*Value calculated from initial cupric nitrate concentration.
Eutro. = eutrophic peat.
Oligo. = oligotrophic peat.
A = electroneutrality ratio.

where (R') and $(R'_2Cu(NO_3)_2)$ are expressed in mmol/g d.w. and (Cu^{2+}) and (NO_3^-) in mM.

A global reaction may be obtained by addition of reactions (6) and (10), assuming the independence of both reaction sites R and R':

$$2RH + 2R' + 2Cu^{2+} + 2NO_3^- \rightleftharpoons R_2Cu + 2H^+ + R'_2Cu(NO_3)_2 \quad (12)$$

with a global apparent constant

$$K = K_1 \times K_2. \quad (13)$$

These equilibrium constants have been evaluated for several metal cations, using the following assumptions:

(1) With an addition of different concentrated metallic solutions (600 mM respectively for each metal cation), i.e. 40 times more concentrated than the usual 15 mM solutions, a saturation of all metal fixation sites is assumed to be obtained for all cations (Pb, Cu, Ca, Mg and Zn).

(2) The total concentration of fixation sites in peat (RH) and R') is assumed to be equal to the amount of cation fixed after reaction with concentrated metal solution (600 mM) at initial pH 3.0–3.3. In fact, 600 mM in nearly the maximum concentration of copper and lead solutions before precipitation occurs at that pH.

(3) For metallic solutions different from cupric ones, mechanisms of metal fixation are assumed to be the same as for copper.

The ion exchange and complexation sites after addition of 15 and 600 mM solution for one of the five selected elements were summarized in Table 5. The homogeneity of fixation sites for these selected metals could be seen from total $(x/m)_0$ values, varying between 4.3 and 5.3 mmol/g d.w. except for the Zn fixation sites on oligotrophic peat (6.8 mmol/g d.w.), implying that the fixation sites are probably the same whatever the metal selected. Besides, maximum amounts of cupric ion exchange sites reach 380 and 260 mmol/kg d.w. with eutrophic peat and oligotrophic peat, respectively; these values are somewhat different to those obtained with Langmuir equation using dried peat: 308 and 101 mmol/kg d.w., respectively (Table 3). Such a difference may be attributed to the difference in peat pretreatment of Table 3 and 5 data, or to the variations in equilibrium pH and ionic strength of both sets of experiments. Table 5 shows also that the maximum amount of sites for oligotrophic peat, i.e. 4.3–5.3 mmol/g d.w., is similar to the values obtained with eutrophic peat, i.e. 4.5–6.8 mmol/g d.w. Thus, both types of peat exhibit equivalent capacity for metal cation fixation, although in raw state they contain very different amounts of metals (Table 1). We observed that, complexation becomes 10 times more important than ion exchange when solution concentration is very high.

Apparent equilibrium constants were calculated from equations (7), (11) and (13) using 30 g d.w./l pre-acidified peat at initial pH 4.0 and 15 mM initial metal concentration. As shown on Table 6, the global affinity of peat metal binding decreases as:

Pb > Cu > Ca > Mg, Zn for eutrophic peat,

Pb > Ca > Cu > Mg, Zn for oligotrophic peat.

Such apparent affinity are significantly larger for eutrophic peat than that for oligotrophic one. It allows a better understanding of large calcium release in eutrophic peat and few calcium release in oligotrophic peat when in contact with cupric ions. It should be emphasized that both the ion exchange (K_1) and complexation (K_2) constants are conditional stability constants since their value may be dependent upon experimental conditions such as pH, ionic strength which varied between 60 and 30 mM before and after equilibrium in this set of experiments, peat

Table 5. Initial and equilibrium conditions for the determination of apparent constants, using 30 g d.w./l pre-acidified peat

Eutrophic peat:									
	15 mM				600 mM				
C_i	pH_i	pH_e	$(x/m)_1$	$(x/m)_2$	pH_i	pH_e	$(x/m)_1$	$(x/m)_2$	$(x/m)_0$
Pb	4	1.93	0.20	0.11	3.2	1.68	0.55	4.09	4.6
Cu	4	2.03	0.16	0.12	3.0	1.88	0.38	4.97	5.3
Ca	4	2.35	0.07	0.12	3.4	2.32	0.15	4.13	4.3
Mg	4	2.37	0.07	0.11	3.3	2.22	0.17	4.33	4.5
Zn	4	2.25	0.10	0.07	3.8	2.07	0.24	4.20	4.4
Oligotrophic peat:									
	15 mM				600 mM				
C_i	pH_i	pH_e	$(x/m)_1$	$(x/m)_2$	pH_i	pH_e	$(x/m)_1$	$(x/m)_2$	$(x/m)_0$
Pb	4	2.30	0.08	0.13	3.2	2.05	0.23	4.23	4.4
Cu	4	2.25	0.09	0.09	3.0	2.00	0.26	4.42	4.7
Ca	4	2.52	0.05	0.17	3.2	2.19	0.15	4.41	4.6
Mg	4	2.52	0.05	0.12	3.2	2.30	0.15	4.97	5.1
Zn	4	2.43	0.06	0.10	3.4	2.39	0.13	6.73	6.8

$(x/m)_1$ = ion exchange capacities in mmol/g d.w.
$(x/m)_2$ = complexation capacities in mmol/g d.w.
$(x/m)_0$ = total fixation capacities in mmol/g d.w., i.e. both ion exchange and complexation sites determined by addition of 100 ml 15 mM and then 600 mM solutions.

Table 6. Apparent equilibrium constants determined for reactions between acidified peat (30 g d.w./l, initial pH 4.0) and different 15 mM metallic solutions: equilibrium pH ranging between 1.9 and 2.5 (see Table 5)

	Eutrophic peat			Oligotrophic peat		
	K_1	$K_2 \times 10^7$	$K \times 10^6$	K_1	$K_2 \times 10^7$	$K \times 10^6$
Pb	9.46	21.4	20.2	2.65	16.4	4.3
Cu	10.77	14.6	15.7	2.91	10.2	3.0
Ca	5.50	15.6	8.6	1.21	32.1	3.9
Mg	4.74	10.8	1.9	1.13	9.8	1.1
Zn	4.17	4.9	2.0	4.48	3.6	1.6
Cu (Coleman *et al.*, 1956) K_1 ($H^+ - Cu^{2+}$) = 2.5*, pH_e 2.7						
Cu (Bunzl *et al.*, 1976) K_1 ($H^+ - Cu^{2+}$) = 0.63†, pH_e 3.2						
Cu (Kadlec *et al.*, 1986) K_1 ($H^+ - Cu^{2+}$) = 1.3‡, pH_e 2.0						

K_1 = ion exchange, K_2 complexation and K global apparent constants [see equations (7), (11) and (13) for definitions].

*Determined with 0.2 g acid-washed Florida peat (no indication on dry or wet weight) shaken for 48 h with 50 ml of solutions containing 0.2, 0.1, 0.06 or 0.02 mmol of $Cu(NO_3)_2$.

†Determined with 1 g acid-treated wet peat added to 200 ml deionized water and addition of 0.005, 0.01, 0.025 and 0.05 mmol of Cu^{2+}.

‡Acid-washed peat (50 g wet peat) added to a measured amount of stirred solution (500 ml) with the equilibrium concentration 0.0–3 mmol/l and pH_e 2.0.

type and concentration. For example, Coleman *et al.* (1956) has found that the complexation constant is dependent on ionic strength and Kadlec and Keoleian (1986) has observed that the ion exchange constant for copper decreased rapidly with increasing pH, indicating the presence of a secondary proton exchange. The results obtained in this work may not exactly represent the reaction mechanism identical to those found in literature (Table 6) since both fixation types are usually poorly discriminated (Coleman *et al.*, 1956) or not observed simultaneously (Bunzl *et al.*, 1976; Kadlec and Keoleian, 1986).

CONCLUSION

Raw peat, either eutrophic or oligotrophic, contains non-negligible amounts of Ca^{2+}, Mg^{2+} and Fe^{3+} but few heavy metals. These metals can be exchanged in the presence of 2 M HCl. This result suggests that these cations can probably participate in ion exchange reactions when peat samples are placed in contact with heavy metal solutions either in soil or in industrial processes.

During fixation of copper ions by both types of raw peat, there exists not only a decrease of pH but also a release of calcium and magnesium. The cupric nitrate fixation by peat seems to incorporate cation exchange and copper complexation, i.e. fixation of the same equivalent of metal cation (Cu^{2+}) and associated anion (NO_3^-): no anion exchange was observed whatever the type of peat. The importance of these two reactions are dependent on cupric concentration applied and also influenced by pH. Besides, complexation reactions become essential when free copper concentration is high, i.e. above 6–14 mM.

Isotherm shows that cation exchange sites are limited (308 and 101 mmol/kg d.w. for eutrophic and oligotrophic peat, respectively, at 30 g d.w./l of peat) whereas complexation sites could not be saturated over free copper concentration ranging between 0 and 15 mM at equilibrium pH ranging between 2.5 and 4.2. This property is especially important to understand the behaviour of peat soils receiving metallic wastes.

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